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EXTINCT NATURAL RADIOACTIVITY: POSSIBILITIES AND POTENTIALITIES

BY
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EXTINCT NATURAL RADIOACTIVITY: POSSIBILITIES AND POTENTIALITIES*

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INTRODUCTION

The discovery of natural radioactivity and the study of its consequences has already had an enormous influence on geology and cosmology. Virtually all quantitative estimates of time in the distant past are based on rates of radioactive transformations, and the energy evolved in such transformations is recognized as an important source of heat in the earth. The abundance of argon in the atmosphere and the occurrence of reservoirs of helium are geochemical consequences of importance. Physical effects of the radiations include the discoloration and the metamictization of minerals and the formation of pleochroic halos, and of still undetermined importance are radiation-chemical effects on organic materials on or within the earth's crust.

All of the effects of natural radioactivity which have been observed so far are due to three of the four classes of natural radionuclides that are defined in the classification given below: namely, *primary, secondary,* and *induced.* A number of writers have speculated on one or more aspects of what may be called *extinct* natural radioactivity, although to date no definite evidence for the occurrence of this fourth type of natural radioactivity has been found. It is the purpose of this paper first to examine thoroughly the possibility of the occurrence of extinct natural radionuclides and of discovering them. Then some consequences of their existence will be discussed, with emphasis on the kinds of information which might be obtained from their discovery and subsequent investigation.

Throughout this paper, certain currently popular views regarding the history of the universe have been adopted in order to give definiteness to the discussion and to permit numerical calculations. Most of what is said is independent of these assumptions, but some of the quantitative conclusions may have to be modified somewhat if these views should prove wrong. One of the objectives of this investigation is to seek means by which some of these ideas might be tested and possibly improved.

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Classification of Natural Radioactivity

It is convenient to classify radioactive nuclides occurring in nature according to the following scheme:

(1) *Primary.* Unstable nuclides occurring naturally at the present time by virtue of the fact that their lifetimes are sufficiently long, relative to the time elapsed since a presumed epoch of large-scale nucleogenesis, for detectable amounts to remain. Those which are known are listed in TABLE 1. It is realized that, in addition, a number of nuclides are *energetically* unstable against decay by one or more of the known modes of radioactive disintegration, but that the *rates* of transformation are so slow that radiations or other evidences of decay have not been

TABLE 1

KNOWN AND PROBABLE PRIMARY NATURAL RADIONUCLIDES

Nuclide	*Type of disintegration*	*Half life (years)*	*References**
U^{235}	α	7.1×10^{8}	3
K^{40}	β^-(89%), ϵ(11%)	1.31×10^{9}	4, 5, 6, 7, 8
U^{238}	α	4.51×10^{9}	9
Th^{232}	α	1.39×10^{10}	
Lu^{176}	β^-	2.2×10^{10}	10, 11
Rb^{87}	β^-	$4–6 \times 10^{10}$	12, 13, 14, 8
Re^{187}	β^-	$\sim 5 \times 10^{10}$	15, 16, 17, 18
Sm^{147}	α	1.25×10^{11}	19
La^{138}	ϵ($\sim$90%), β^-($\sim$10%)	$\sim 2 \times 10^{11}$	20
Pt^{190}	α	$\sim 5 \times 10^{11}$	21
W^{180}**	α	$\sim 3 \times 10^{14}$	22
In^{115}	β^-	$\sim 6 \times 10^{14}$	
Nd^{144}	α	$\sim 3 \times 10^{15}$	23, 21, 17
Bi^{209}	α†	$\sim 2 \times 10^{17}$	25, 26
Cd^{113}	β^-	$> 10^{15}$	20
In^{113} or	ϵ	$> 10^{14}$	27
Sb^{123} or	β^-	$> 10^{13}$	20
Te^{123}	ϵ	$> 10^{13}$	27, 20
Ta^{180}	β^- or ϵ	$> 10^{12}$	28, 29, 30
V^{50}	ϵ	$>3 \times 10^{15}$	27, 31, 20
Zr^{96}	β^-‡	$>2 \times 10^{16}$	20
Ca^{48}	β^-	$>2 \times 10^{16}$	
Te^{130}	β^-	$\gtrsim 3 \times 10^{21}$	32

ϵ This symbol indicates electron capture.

* Most of the data in this table are given, with documentation, by Hollander, Perlman and Seaborg[1] or by King.[2] This column lists references not recorded in either of these summaries.

** The mass number is uncertain; see text.

† There is some doubt[26] concerning the reality of the activity reported.[24,25]

‡ There is some uncertainty that the nuclide in question is energetically unstable.

detected. From an empirical point of view, such nuclides may be regarded as stable, and virtually all of their atoms originally created are still extant. TABLE 1 includes a number of apparently stable nuclides that are believed from mass relationships to be *beta* unstable, with experimental lower limits to their lifetimes. The number of naturally occurring nuclides that are *alpha* unstable, but of very long lifetimes, is considerably greater.[33] Such nuclides whose alpha activity has not been observed are not included in the table. The table does include Bi^{209}, for which alpha activity has been reported by two groups[24, 25] but denied by a third.[26] Also included is the alpha activity of tungsten, recently discovered by Porschen and Riezler.[22] Although they believed it due to a rather short-lived and extremely rare isotope, it is felt here that a more reasonable assignment is to W^{180}, and the half life has been calculated accordingly. The most recent additions to this class are Nd^{144}, whose alpha activity was discovered in this laboratory by Waldron, Schultz, and the writer[23] and confirmed by Riezler and Porschen,[21] and Pt^{190}, discovered by the latter team.[21] Nuclides that are energetically unstable against *double beta* disintegration are not included. Although their number is large, the occurrence of this type of transformation has not been conclusively demonstrated.

(2) *Secondary.* Relatively short-lived nuclides that occur in nature as a result of continual formation by transformation of primary natural radionuclides. All that are known at present are members of the three disintegration series originating with U^{238}, U^{235}, and Th^{232}, but others may soon be added to the list. For example, Ca^{48} is probably capable[35,36] of negatron decay to Sc^{48}, which has a half life of 44 hours and decays to Ti^{48}. In a large mass of calcium there is probably a considerable number of atoms of Sc^{48} in secular equilibrium with its parent. An observation of excess Xe^{130} in ancient tellurium minerals has been interpreted as an indication of instability of Te^{130} toward double beta disintegration.[37, 32] However, Te^{130} is probably unstable towards ordinary beta disintegration,[20] and if this is the process leading to Xe^{130} formation, there should be traces of 12.5-hour I^{130} associated with tellurium as a secondary natural radionuclide. It is likely that several such two-membered radioactive chains exist in nature, and the extraction of the daughter from a large quantity of the parent provides an extremely sensitive method for the detection of the activity of the latter.[35] The radioactive products of spontaneous fission of uranium[38] might also be considered in this class.

(3) *Induced.* Relatively short-lived nuclides that are found in nature as a result of continual production by nuclear reactions. The best-known example is C^{14}, produced in the atmosphere by the absorption in nitrogen of cosmic ray neutrons. The terrestrial hydrosphere contains some H^3,

resulting from the ejection of tritons from atmospheric nuclei by primary and secondary cosmic rays. In uranium and thorium minerals are found Pu^{239}, Np^{237}, and U^{238}, which are formed by the action of neutrons from spontaneous fission and (α, n) reactions. Induced fission products also occur in such minerals,[38] and presumably a number of other neutron-induced radioactivities could be found there by a careful search. Be^{7} produced by cosmic rays in the upper atmosphere has recently been observed in rain water by Arnold,[39] and it has been predicted that Be^{10} should be detectable in deep-sea sediments.[28,40] Davis and Schaeffer have detected Cl^{36} produced in rocks at high altitudes by cosmic-ray neutrons.[41] A search has been initiated for radioactivities induced in meteorites by cosmic-ray primaries and secondaries.[42]

(4) *Extinct.* Unstable nuclides whose lifetimes are too short for detectable amounts to have persisted from the time of nucleogenesis, yet long enough for their decay to have produced effects in nature which can be identified at the present time.

EXTINCT NATURAL RADIOACTIVITY

Possible Manifestations of Extinct Natural Radioactivity

The most likely way in which the past existence in nature of an extinct radioactivity could be detected would be by the finding of its decay product in abnormal abundance in a portion of matter, such as a mineral or a geochemical phase, that once had contained the unstable nuclide. Thus a reasonable fraction of the nuclide would have to have survived the interval from nucleogenesis until the chemical fractionations leading to the formation of the phase in question.

The earliest separations of elements were probably those of the volatile from the nonvolatile ones as the cooling of matter permitted the formation of condensed phases. Such separations on a large scale occurred in the formation of the planets, including the earth. The near absence of the heavy noble gases from the earth indicates that they must have been separated from it during or shortly after its formation. Suess[43] has examined critically the isotopic composition of terrestrial xenon from the point of view of a possible abnormal amount of Xe^{129} resulting from the decay of the long-lived I^{129}. He considered the Xe^{129} abundance not abnormal. On the other hand, Katcoff, Schaeffer, and Hastings,[44] who measured the I^{129} half life to be 1.7×10^{7} years, considered the Xe^{129} abundance to be abnormally high, and attributed the excess to decay of I^{129} persisting after the loss of the major part of the xenon from the earth. Since this point of view has been objected to strongly by Suess and Brown,[45] it cannot be considered as established that I^{129} is an extinct natural radionuclide.

Suess[43] also discussed the relative isotopic abundances of the decay products of the long-lived nuclides Se^{79} and Pd^{107} in terrestrial bromine and silver, concluding them both to be normal in materials that have been examined. However, measurements do not exist on materials in which adequate geochemical fractionation might have occurred. Moreover, the lifetime of each of the nuclides mentioned is now known to be less than 10^7 years, so that no such effects are to be expected in terrestrial materials.

Brown[46] has proposed that a search be made for elements with abnormal isotopic composition in meteorites, to enable the placing of upper and lower limits on the time elapsed between the formation of the elements and their fractionation in the parent body of the meteorites, from the presence or absence of decay products of intermediate-lived nuclides in amounts greater than normal. The only significant measurement of this type made so far is that of Wasserburg and Hayden,[47] who looked for radiogenic Xe^{129} from I^{129} in a chondrite meteorite. From its absence, they obtained a lower limit of 2 to 4×10^8 years for the interval between nucleogenesis and the last crystallization of the meteorite.

It might also be possible to detect extinct natural radioactivity in terrestrial minerals. The greater time that was probably required for the formation of accessible minerals, as compared to that for the separation of the phases composing meteorites, would tend to render terrestrial minerals less favorable than meteorites. On the other hand, a much greater variety of minerals is to be found in the earth's crust than in meteorites, and chemical fractionations of the requisite type are here much more common and often more complete. This consideration tends to favor terrestrial materials. A few reports of the occurrence of the decay product of an extinct radionuclide in terrestrial matter have been made, but none have been substantiated. Many years ago Strutt (later Lord Rayleigh) found anomalous amounts of helium in beryls,[48] the amount apparently being correlated with mineral age,[49] and suggested[48, 50] that the origin might be a now-extinct alpha emitter, possibly an unknown isotope of beryllium (perhaps Be^8). However, Fay *et al.* have shown[51] that this hypothesis is quantitatively incompatible with the data. Wahl[52] claimed to have observed mass-spectrographically barium consisting essentially of Ba^{132} isolated from a 10^9-year-old specimen of the cesium mineral pollucite, and attributed this to the previous presence of a now-extinct Cs^{132}. However, Hahn *et al.*,[53] attempting to reproduce this observation, found that the barium isolated from a similar specimen from the same locality gave a normal mass spectrum, and attributed Wahl's results to artifact ions in the mass spectroscope. Inghram and Reynolds[37] obtained an indication of excess Xe^{129} in a 10^9-year-old tellurium mineral, which they thought might be due to the decay of I^{129} originally present in the mineral. However, no excess Xe^{129} could be found in the more careful measurements of Hayden and Inghram.[32] As will be shown, the half-life of 1.7×10^7 years is too short for any I^{129} to be present in terrestrial minerals. Cooley *et al.*[54] have proposed that variations in the relative amounts of zirconium and hafnium in nature might be explained by radioactive parents that were more easily separated and that have now disappeared. Such an explanation is as unreasonable as it is unnecessary.

A different type of manifestation of extinct natural radioactivity might result from its energy evolution. That now-extinct radionuclides may once have been present in the earth and have contributed to its internal heat has been suggested frequently, but usually uncritically.[55] In a provocative paper, Rosenblatt[56] has discussed qualitatively the effects, principally thermal, of a primeval endowment of U^{236}. This particular nuclide has a half life of only 2.4×10^7 years,[57] and it is shown below that this is probably too short for ascribable influence on the thermal history of the earth. Urey[58] has suggested that the recently discovered[59] Al^{26}, whose half life is $\sim 10^6$ years, might have been responsible for heating the bodies from which the meteorites were derived. This implies a fairly rapid formation of these bodies after the formation of the elements, which seems unlikely. Such considerations might be important if there should exist a nuclide with a somewhat longer lifetime than Al^{26} and U^{236}, especially if it had a moderately high primordial abundance. Nevertheless, even though such an extinct nuclide might have had important geothermal effects, it would be difficult if not impossible to detect and ascribe them without a prior knowledge of the nuclide and its half life.

The same is true of other effects of energy evolution, such as radiation damage and pleochroic halo formation. Joly, one of the foremost investigators of the latter phenomenon, has attempted to attribute halos of anomalous radius to natural alpha emitters that are now extinct,[60] but it has been impossible to obtain conclusive evidence for this point of view.[61] Thus it seems that, as far as original detection of an extinct natural radionuclide is concerned, the examination of isotopic abundances offers the greatest hope.

Probable Range of Half Lives for Extinct Natural Radioactivities

For the purposes of this discussion, a prevalent point of view is adopted that the universe, or at least the present phase of its existence, was created at an instant several billions of years in the past, and all nuclides moderately close to stability were formed in amounts comparable to their stable neighbors in this creative event. The upper limit for the half life of an extinct natural radioactivity should be the same as the lower limit for a primary natural radioactivity. For definiteness, we may use as the limit that half life yielding a decay factor of $\sim 10^{-8}$ during the lifetime of the universe. The half life is then ~1/27 of the latter period. Since we wish an upper limit to the half life, an upper limit to the age of the universe must be used in the calculation.

Such an upper limit can be arrived at from a consideration of the lifetimes and extant amounts of the shortest-lived primary natural radionuclides, as has been done on several occasions.[43, 46, 62, 63, 64, 65] The shortest-lived member known is U^{235}, whose half life is 7.1×10^8 years, and which has an abundance of 1/138 that of U^{238}, of half life 4.5×10^9 years. Houtermans[65] considers that U^{235} probably was never more abundant than U^{238}. It is difficult, however, to estimate the original ratio of U^{235} to U^{238}, since uranium is separated from the stable nuclides by a region including many short-lived nuclides, and the mechanism of nucleogenesis may have resulted in a distribution here not partaking of the regularities found to some extent in the lighter elements.[66] We may feel reasonably certain, however, of an estimate of Wefelmeier[63] that the primordial U^{235}/U^{238} ratio was at most 10/3. This gives an upper limit of 7.5×10^9 years.

The next shortest-lived nuclide, K^{40}, has a half life of 1.31×10^9 years and a present isotopic abundance of 0.0119 per cent. Suess[64] believes that K^{40} probably never exceeded 1 per cent of the abundance of potassium. From this may be calculated an upper limit to its age of about 8.4×10^9 years.

Another upper limit is given by the relative cosmic abundances of U^{235} and its decay product, Pb^{207}.[43, 67, 68, 69] The cosmic abundances of elements are very imperfectly known, but a ratio can be estimated from the analytical data on meteorites of Patterson *et al.*[70] In a chondrite meteorite they found the weight ratio $Pb/U \sim 80$ and the isotopic ratio $Pb^{207}/Pb = 0.21$, whence the atomic ratio $Pb^{207}/U^{235} \sim 3 \times 10^3$ at present. Since not all of the Pb^{207} can have been derived from U^{235}, the transformation must have been proceeding for a time less than about 8×10^9 years.

Thus, it is seen that we have to admit the possibility that the universe is as old as $\sim 8 \times 10^9$ years, even though this is somewhat higher than is currently held likely. This gives as the upper half-life limit for extinct natural radioactivity $\sim 3 \times 10^8$ years.

The dividing line between the half lives of extinct and primary natural radioactivities is, of course, not sharp, because the extant amount of a radionuclide depends not only on the decay factor but also on the amount originally present. Moreover, the limit of detection depends not only on the amount present but on the relative amounts of stable isotopes, on the type of radioactivity, and on the sensitivity of detection methods, which are constantly being improved. FIGURE 1 shows the present specific activity of an element containing a long-lived radioisotope as a function of its half life and its primordial isotopic abundance relative to the present total quantity of the element. A molar basis is used here, instead of the conventional weight basis, in order to permit

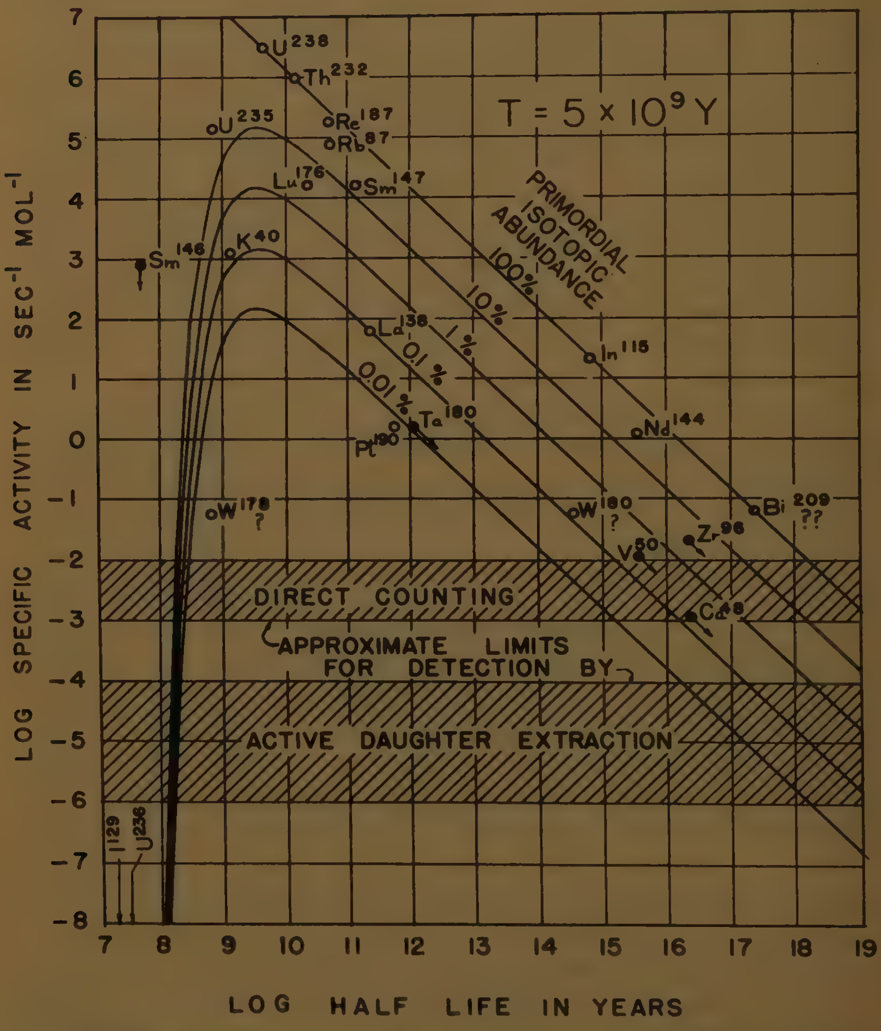

FIGURE 1. Present molar specific activity of primary natural radioelements as a function of half life and primordial abundance of unstable isotope. The points are from experimental data. The curves are calculated assuming an age of 5 × 10^9 years for the universe.

a single plot to accommodate all elements. The curves are calculated for an age of the universe of 5×10^9 years. The circles represent all of the known primary natural radioactivities, and the dots attached to arrows represent limits for the indicated nuclides. In the absence of stable isotopes, the specific activity does not change with time, and is inversely proportional to the half life. Th^{232} and Bi^{209} are examples. In most cases, however, stable isotopes are present, and the curves each exhibit a maximum specific activity at a value of the half life approximately equal to the age of the universe. For longer half lives, decay is relatively unimportant, and the specific activity falls off in inverse proportion to the half life. For shorter half lives, decay is the preponderant factor, and the specific activity falls off very rapidly as the half life becomes shorter than ~1/10 of the age of the universe. It is conceivable, of course, that a nuclide having a lifetime close to the division between extinct and primary natural radioactivity might first be classified in the former category and, later, when more powerful methods of detection were brought to bear on it, be found to be in the latter class. However, a primary natural radionuclide that is close to the limit for extinction would share much of the interest and importance of one that is truly extinct.

A lower limit to the half life for an extinct radionuclide which would enable it to be classifiable as natural is somewhat more difficult to evaluate. This is principally because we have no definite knowledge of the age of the universe at the time when chemical separations yielding fractions now accessible to us began to occur. If the universe is actually as old as the upper limit given above, 8×10^9 years, and if the oldest dates yet determined for meteorites, 4 to 5×10^9 years,[71] represent a limit to the antiquity of materials that can ever be obtained for examination, then the age in question might be as long as 3 or 4×10^9 years. It is likely, however, that the universe was very much younger when chemical separations that might be useful to us now took place.

If the age of the elements is the same as the age of the universe, astronomical estimates of the age of the latter will be pertinent. For two decades the expanding-universe interpretation of the Hubble law of the red shifts of the extragalactic nebulae in terms of recession velocities has been considered to yield an expansion time of about 1.8×10^9 years. This time is proportional to the scale of distances to the nebulae. Behr[72] indicated the need of a revision of the criterion for evaluating relative distances of distant and near-by nebulae from their apparent magnitudes, which would approximately double the distance scale. Baade[73] discovered an error in the chief distance indicator for the near-by nebulae, requiring that their distances be approximately doubled, and this has been amply confirmed.[74] Baade's latest correction factor for the distance to near-by systems is 2.3.[75] Improvements in photometry, magnitude scales, and identifications of indicators of relative distances of near-by and moderately distant nebulae have also led to an upward revision of the distance scale for objects in the latter class, with an over-all correction factor of >2 to ~4.[76] Also, a great many new brightness and red-shift measurements have been made on faint nebulae, and better selection criteria have been developed, with the result that a reliable value for the Hubble constant is to be expected in the near future. Sandage[77] has made a preliminary analysis of all data available in 1954, and concludes that the most probable correction factor to Hubble's result is about 3, giving an expansion time of $\sim 6 \times 10^9$ years. However, the uncertainties are still such that a time of 7 or 8×10^9 years is not excluded. It has been pointed out, moreover, that even if the Doppler interpretation of the red shifts is accepted, the calculation of the expansion time is not straightforward, and different cosmological models will yield different times.[78]

Ter Haar[79] has recently surveyed astronomical evidence on the ages of various objects in the universe. Unfortunately, most conclusions from stellar and nebular dynamics are only approximate, and refer to systems that may be younger than the universe as a whole. Recently, the theory of thermonuclear reactions in stars and stellar evolution has yielded some fairly precise ages for certain star clusters. Sandage[80] has derived an age of 5.1×10^9 years for the stars in two globular clusters, and Hoyle and Schwarzschild[81] have estimated the age of a globular cluster as $(6 \pm 2) \times 10^9$ years. Johnson and Sandage[82] have found 5×10^9 years for an open galactic cluster, with an indication that there are no older stars in the solar neighborhood. It is possible that the stars in these groups were among the first to be formed, and have an age close to that of the elements and the universe. Accordingly, we may already have in the 4.5×10^9-year-old meteorites materials resulting from chemical separations that occurred when the universe was considerably less than a billion years old.

It would be desirable to have a direct estimate of the age of matter when the meteorites and other objects were formed, rather than to rely on a difference. According to some current views, early in the history of the universe a series of condensations gave rise to the galaxies, stars, planets, and other bodies. Solid objects were or became hot, and chemical fractionations occurred. Estimates of the time elapsed between nucleogenesis and the cooling and condensation of matter to form planets have been made, particularly by Gamow,[83] whose estimate is a few hundred million years. This probably gives us the lower limit to the period in question. If the observation of Wasserburg and Hayden[47] refers to this same time, their lower limit of 2 to 4×10^8 years is consistent.

The decay factor which can be tolerated by a nuclide before it will have been reduced to an amount insufficient to produce lasting effects is considerably larger than the 10^{-8} given for present detection. The sensitive methods of radioactivity detection cannot be employed, and the stable decay product will probably have to be identified and measured in the presence of a quantity of the same nuclide of primordial origin. This factor in favorable cases might be as small as 10^{-6}, but in unfavorable cases might have to be as large as 10^{-1}. For purposes of calculation we have taken as a representative value of the factor $\sim 10^{-3}$, and as the minimum age of the universe at the time when presently accessible chemically fractionated materials were formed $\sim 3 \times 10^{8}$ years. The corresponding half life, which may be taken as a lower limit to the range of half lives for extinct natural radionuclides, is $\sim 3 \times 10^{7}$ years.

In summary, the probable range of half lives for extinct natural radionuclides is from $\sim 3 \times 10^{7}$ to $\sim 3 \times 10^{8}$ years, or within a factor of about 3 of 10^{8} years. Visualization of the situation may be facilitated by an inspection of FIGURE 2, which shows the fraction of the primordial amount of a radionuclide remaining at any time since the origin of the universe, as a function of its half life.

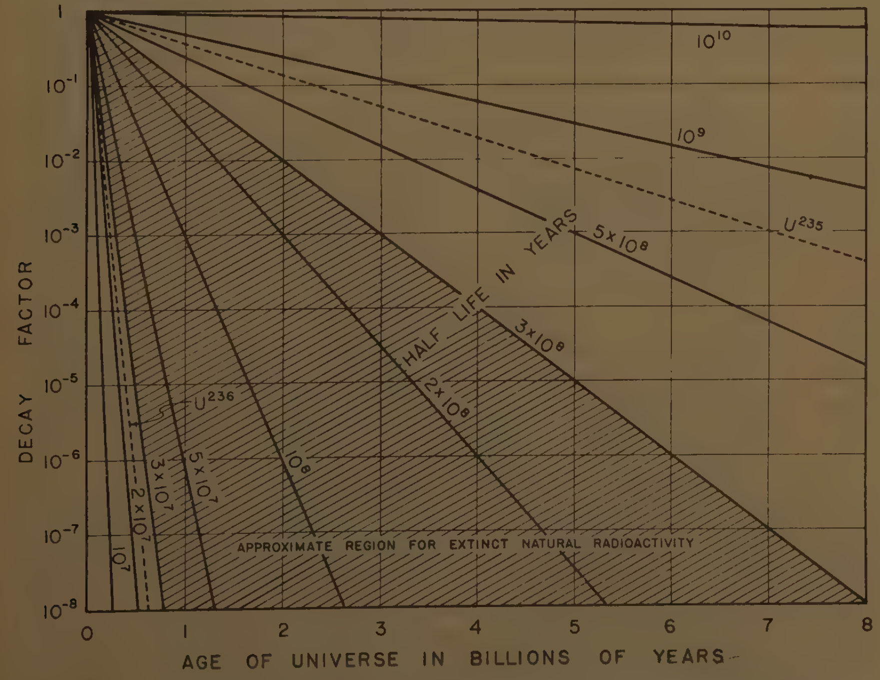

FIGURE 2. Fraction of primordial radionuclides remaining at various times after their creation as a function of half life.

POSSIBILITY OF EXISTENCE OF EXTINCT NATURAL RADIONUCLIDES

Survey of Known Long-Lived Nuclides

In order to estimate the likelihood of the existence of undiscovered nuclides having half lives within a factor of 3 of 10^8 years, it is useful to examine the occurrence of long-lived nuclides on either side of this range. FIGURE 3 exhibits in graphic form all presently known nuclides with half lives greater than 10^4 years. For reasons that will be apparent later, a differentiation has been made between beta-unstable and alpha-unstable nuclides.

It is to be noted that, with the possible exception of the recently discovered Sm^{146}, whose half life is only very roughly known,[84] there is no known nuclide whose half life lies between those of U^{236} and U^{235} As will be shown later, U^{236} (half life 2.4×10^7 years) represents an unfavorable case, and may be considered to lie definitely outside of the region in question. U^{235} (half life 7.1×10^8 years) is considerably outside of the region in the opposite direction. Decay curves for these two extreme nuclides have been included in FIGURE 2.

If there should exist nuclides with suitable lifetimes, the reasons for their not having been discovered hitherto are readily apparent. Their absence in nature now prevents use there of the sensitive methods of radiation detection. On the other hand, because of their very low specific activity relative to most artificially produced radionuclides, their detection as products of nuclear reactions is quite difficult.[46] In view of these facts, it is quite possible for such nuclides to exist without having yet been discovered.

Expectation Number of Extinct Natural Radionuclides

An examination of FIGURE 3 suggests that there is a gap in the vicinity of 10^8 years which is somewhat wider than it should be. On the basis of the frequency of half lives on both sides of this gap, it seems likely that there should be at least one and possibly several half lives within the range for extinct natural radioactivity. This appears to be particularly so for the beta-active nuclides.

A detailed analysis of the statistical distribution of lifetimes of all known beta-labile nuclides within several classes that are close to stability is being made by Jones and Brightsen in collaboration with the author.[85] This kind of survey has the advantage over previous lifetime surveys[86] that one is dealing with a closed group of nuclides whose total number is known. This group, moreover, contains all of the nuclides having long beta-disintegration lifetimes. Of the total number of about 550 members of this group, about 65 per cent are known, leaving ap-

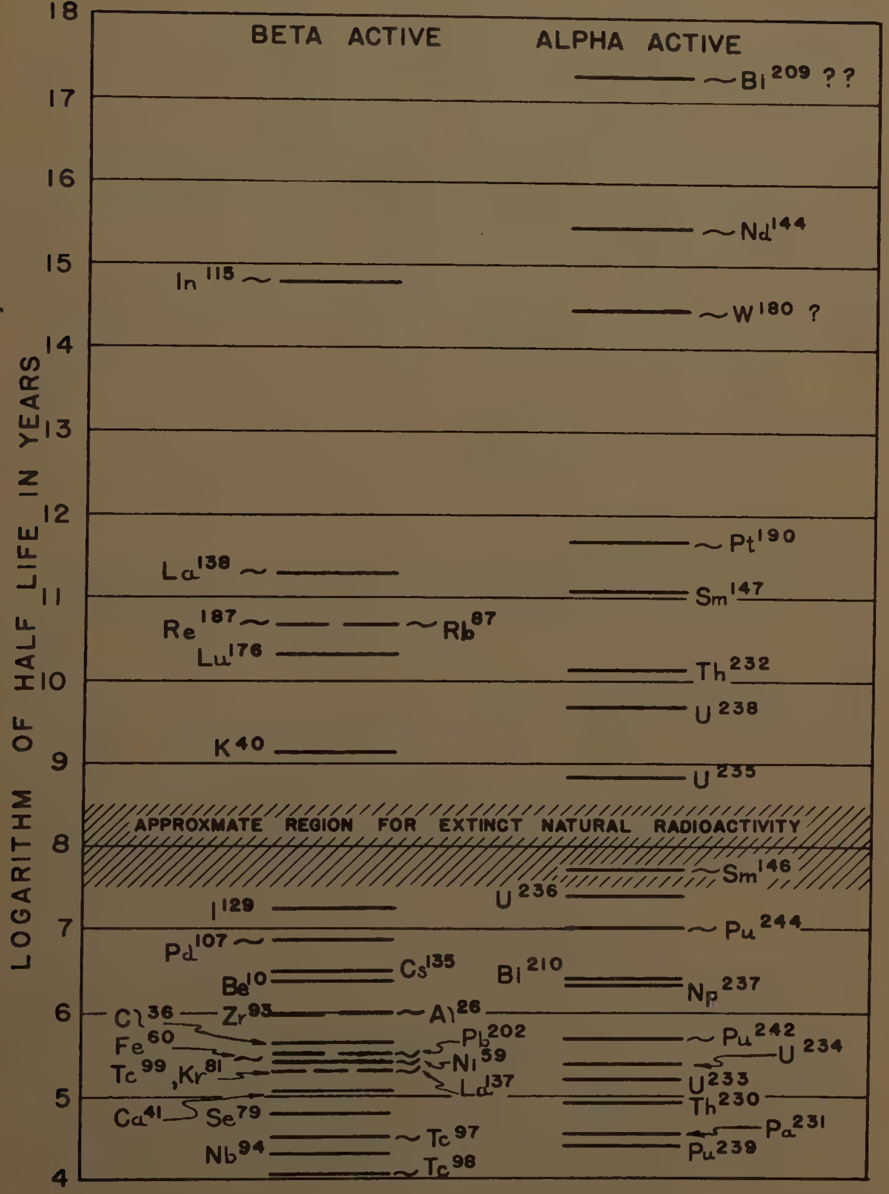

FIGURE 3. Survey of known long-lived radionuclides, arranged according to half life. The symbol "$\sim$" indicates that the half life is known only approximately. The symbol "?" indicates an uncertainty in the mass number. The symbol "??" indicates uncertainty about the existence of the activity reported.

proximately 190 yet to be discovered. If one attempts to enclose the histogram of the frequency as a function of the logarithm of the half life for the known members of the group with a smooth curve whose integral is the total number in the group, the curve obtained indicates that there should be ~2 half lives between 3×10^7 and 3×10^8 years.

Of course, in dealing with such small numbers, statistical conclusions are subject to considerable uncertainty, and it is quite possible that the actual number is zero. The possibility of real gaps in the complete distribution curve should not be ruled out. It is fairly certain that no beta-active nuclide exists between K^{40} and Lu^{176}, which span a region somewhat broader than that of interest here. However, there is a general increase in the frequency of half lives on going to shorter times, so that it is probably unlikely that there exists no half life within the region of interest. This conclusion is strengthened by the discussion of comparative half lives in the next section.

Possible Types of Extinct Natural Radionuclides

The alpha emitters do not offer as great a hope for including extinct natural radionuclides as those which are beta active. Alpha activity is most common in the elements above lead, and all nuclides in that region have as ultimate stable or long-lived decay products one of the following: Pb^{204}, Pb^{206}, Pb^{207}, Pb^{208}, Bi^{209}, Th^{232}, U^{235}, and U^{238}. Identification of an excess of any lead isotope as the decay product of an extinct radioactivity would be quite difficult because of the large variations in isotopic composition of natural lead samples. Identification of radiogenic Th^{232} would be impossible because of the fact that this nuclide has no stable or long-lived isotope. For this reason, U^{236} is a particularly unfavorable case. A nuclide decaying to U^{235} or U^{238} might result in a detectable change in the isotopic composition of uranium, but it is not very probable that a sufficiently long-lived ancestor of U^{235} or U^{238} exists. The most likely prospect in the entire heavy element region is Pu^{244}, which is predicted to have an alpha half life of ~ 10^7 years and is expected to be beta stable.[87] Since it would transform to Th^{232}, decay product detection would be impossible. However, if its half life is close to 10^8 years, it may have had important early thermal effects.

The other region of nuclides in which alpha activity with lifetimes near the requisite magnitude has been observed is in the midst of the rare earth elements. Here adequate chemical fractionations probably do not occur anywhere in nature. For this reason, it might not be possible to detect the past existence of Sm^{146} even though its half life should be of the optimum order of magnitude. Its decay product, Nd^{142}, has an isotopic abundance of 27.1 per cent and, considering the probable high proportion of neodymium in any natural samarium-containing material, it would completely swamp any radiogenic Nd^{142}

Alpha activity has been predicted to be an important mode of radioactive decay for nuclides sufficiently far to the neutron-deficient side of the line of beta stability for the entire region from the rare earth elements to lead.[33] Artificial alpha activity has been produced in gold and mercury, as well as in the rare earth region.[88] In one case, Gd^{150}, a nuclide which is apparently beta-stable[35, 89] but is missing in nature has been found to be an alpha emitter[88] which, though its half life is $> 10^5$ years,[89] is cosmologically short-lived. A number of long-lived alpha emitters occur in this region (TABLE 1), and it is conceivable that an intermediate-lived alpha emitter may be found here. The natural activity of tungsten, discussed below, is a case in point, but the discussion will show that the possibility of an extinct natural alpha emitter in this region is small.

It is possible, of course, that extinct alpha emitters might have been important contributors to the heating of the earth and to the helium content of meteoritic and terrestrial materials. However, because these effects would be intermingled with similar effects of other nuclides, their identification with particular extinct nuclides would be difficult if not impossible unless unambiguous characterization through product recognition could be achieved.

It is thus apparent that any discoverable extinct natural radionuclide will most likely decay by beta disintegration. Moreover, it is possible to indicate the types and characters of beta transformations that might be involved. Positron emission can be eliminated as virtually unimportant, since any long-lived positron emitter would probably decay much more rapidly by electron capture. Thus the decay must be by electron capture or negatron emission, depending on which side of the beta-stability region the nuclide occupies. There is also the possibility of dual decay by both of these processes for nuclides lying between beta-stable isobars.

It is well known that the comparative half lives (*ft* products) of beta transitions tend to cluster into groups for the various types of allowed and forbidden disintegrations.[90] Within each group there is a spread of two or three powers of 10, and, because of variations in energy and in nuclear charge, the spread of actual lifetimes covers four to six powers of 10. It is pertinent to inquire whether any of these distributions overlap the region about 10^8 years $\approx 3 \times 10^{15}$ seconds.

For negatron emitters, representative comparative half lives for various degrees of forbiddenness are as follows:

Allowed:	$\sim 10^5$ seconds	$\approx 3 \times 10^{-3}$ year
First forbidden:	$\sim 10^7$ seconds	$\approx 3 \times 10^{-1}$ year

Second forbidden:	$\sim 10^{13}$ seconds	$\approx$	3×10^{5} years
Third forbidden:	$\sim 10^{18}$ seconds	$\approx$	3×10^{10} years
Fourth forbidden:	$\sim 10^{22}$ seconds	$\approx$	3×10^{14} years

Since a high energy results in a relatively low lifetime and vice versa, it appears that third-forbidden transitions of high energy or second-forbidden transitions of low energy might have the requisite lifetimes.

The shortest-lived third-forbidden negatron emitter is K^{40}, and it owes its relatively rapid decay to its high disintegration energy, 1.33 Mev. A third-forbidden negatron transition of similar disintegration energy and higher atomic number, or of low atomic number and higher energy, might have the correct rate of decay (other things being equal, an increase in atomic number increases the rates of both negatron emission and electron capture). However, a necessary condition is that there be no other nuclear state of the daughter to which a transition can occur more rapidly. Because the density of states is fairly high for most heavy nuclei, this condition probably could be met only among the light elements, and even there the probability of meeting simultaneously the conditions of spin change (3 or 4), parity change (yes), and energy (~1.5 Mev) is very low.

The longest-lived second-forbidden negatron emitter known is I^{129}, whose maximum beta energy is 0.15 Mev. A similar energy in a lighter element, or a somewhat lower energy in a heavy element, might well yield a lifetime sufficiently long for our purposes. The existence of negatron emitters having the requisite spin change (2 or 3) and parity change (no) and of very low disintegration energy is considered quite likely.

In principle a less highly forbidden transition could have a very long lifetime if its energy is extremely low, and Re^{187} seems to be such a case. Dixon and McNair,[17] using a proportional counter, were unable to detect the natural activity of rhenium reported by Libby and collaborators[91] using a Geiger counter. Suttle and Libby[16] reconfirmed the activity, but found that the radiations were extremely soft, the maximum negatron energy being less than 8 kev. They indicated the need for a severe downward correction of their previous half life, 4×10^{12} years, to $< 10^{11}$ years. Hintenberger *et al.*[92] observed radiogenic Os^{187} in a rhenium-rich molybdenite, and estimated the half life as $\sim 5 \times 10^{10}$ years.[15] The apparently discrepant observation of Dixon and McNair might be explained[8] if the maximum particle energy is less than 1 kev, the bias level of their counter. Rightmire *et al.*,[18] using a proportional counter at lower bias, have observed electrons with energies somewhat below 500 ev. The measured spin of Re^{187} is 5/2, and Klinkenberg's[93] odd-nucleon configuration assignments of $d_{5/2}$ for Re^{187} and $p_{1/2}$ for Os^{187} give spinparities of 5/2+ and 1/2– respectively, whence the transition should be first forbidden. It is only because the available energy is so exceedingly small that Re^{187} is a primary natural radionuclide. A similar nuclide of slightly higher energy could well have a half life of $\sim 10^8$ years. However, the requisite energy range is extremely narrow, so that the probability that a first-forbidden transition has just the right energy is quite small.

Very little information exists on forbidden electron-capture transitions. However, the meager data available do suggest strongly that their comparative half lives are much longer than those for negatron emission of the same order of forbiddenness, when, as is customary, the *f* functions for allowed transitions are used in the computations. Thus, the definitely first-forbidden[94] electron-capture decay of K^{40} has a comparative half life in the range of those for second-forbidden negatron emitters. Its value cannot be computed because the transition energy is not known accurately enough, but from the fact that an appreciable fraction of the electron captures involve the K-shell,[95] an extremely low energy can be eliminated as an explanation of the long lifetime. The electron capture decay of La^{138} is probably second forbidden,[20] yet this transition is not very much more rapid than the fourth-forbidden negatron emission by the same nuclide.[96] The adjacent isobars Sb^{123} and Te^{123} have spin-parity of 7/2+ and 1/2+, so that the transition between them should be second-forbidden, yet careful measurements by Selig[20] have been unable to reveal activity in either nuclide. A possible explanation is that Te^{123} is the unstable isobar, and that its electron capture rate is quite low relative to those for second-forbidden negatron emission. Another possibility in this and other cases is that the energy available for electron capture might be less than the K-shell binding energy, so that only L- or higher-shell electrons could be captured. The electron density of such electrons at the nucleus is low, so that the capture would be correspondingly slow.

The conclusion to be drawn from this discussion is that electron-capture transitions of very low disintegration energy and first-forbidden character (spin change 1 or 2, parity change yes), or of moderate energy and second-forbidden character, might well possess appropriate lifetimes for extinct natural radioactivity, but that third-forbidden transitions would probably be too long-lived. It seems quite possible that nuclides possessing the required characteristics might exist.

Some Specific Possibilities

In 1948 the writer published[35] a "beta stability diagram," from which the degree of stability or instability of a nuclide can be determined approximately by inspection. Although the "limits of beta stability" were determined imperfectly by the data then available, it was possible to list a number of nuclides that were apparently just outside of the limits and that accordingly should have low disintegration energies, if, indeed, they were outside the limits. Many of these nuclides have subsequently been characterized, and half lives ranging from a few days upward to that of I^{129} have been found (in three cases, Pt^{190}, Dy^{156}, and Gd^{150}, the nuclide has been found to be beta stable). A number of the nuclides listed have not yet been observed, in spite of searches for some of them. These are the chief possibilities for extinct natural radioactivity, especially since the failure to find some of them has been due to their long lifetimes. The shifting of the line and limits of beta stability as the result of new data and of recent theoretical concepts, particularly that of nuclear shell structure, has suggested several additions to the list. Considerations of different nature add a few more, and there is a definite possibility that a very long-lived radionuclide may turn up without being expected. In the following paragraphs a number of nuclides which are expected to be long-lived are discussed, grouped according to type of radioactivity.

(1) *Alpha emitters*. As mentioned earlier, Sm^{146} and Pu^{244} might possess lifetimes of the correct magnitude, but would be difficult or impossible to identify as extinct radioactivities. For a while it was thought that Pb^{202} was beta stable and owed its absence in nature to alpha instability,[97] but this nuclide has recently been found to undergo electron capture with a half life of $\sim 3 \times 10^5$ years.[98]

Porschen and Riezler,[22] who found the natural alpha activity of tungsten, determined an approximate energy of the alpha particles from their measured range in nuclear emulsions, and from the result (3.2 Mev) calculated a half life of $\sim 6 \times 10^8$ years. From the observed specific activity it followed that the responsible isotope must have an isotopic abundance of $\sim 3 \times 10^{-9}$. The most likely mass number was considered to be 178. If this interpretation is correct, W^{178} might represent a case of nearly extinct natural radioactivity. In 5×10^9 years the decay factor for the given half life would be $\sim 10^{-3}$. If, however, the primordial isotopic abundance of W^{178} were similar to that for analogous cases, $\sim 10^{-4}$, the decay factor would be $\sim 10^{-5}$. The half life would then be $\sim 3 \times 10^8$ years, just on the border between extinct and primary natural radioactivity. W^{178} would then have much of the importance of an extinct natural radioactivity, with the additional advantage that the amount present as a function of time in the past could be calculated from the amount still remaining. Many tungsten minerals should be essentially free of hafnium, and the low isotopic abundance of the potential decay product, Hf^{174}, 0.20 per cent, would further facilitate the detection and measurement of radiogenic Hf^{174}. This important possibility should be looked into, and an investigation to establish the mass number of the active tungsten isotope is in progress.[99]

W^{178} and other possible light isotopes, however, have been fairly definitely characterized as short-lived beta disintegrators.[1] It is, of course, possible that the known 21.5-day W^{178} is an excited isomer of a previously undetected ground state. But such a short-lived alpha activity of W^{178} would imply, according to semiquantitative calculations,[33] detectable alpha activity in W^{180} at about the level observed. A modest and easily possible correction to the reported alpha particle energy would make it correspond nicely with the half life given for W^{180} in TABLE 1, without the necessity of postulating an unknown isotope. A similar argument makes it seem unlikely that there can be any beta-stable nuclide in the region from the heavy rare earths to lead with an alpha half life of $\sim 10^8$ years. It would have to be the lightest beta-stable isotope of an even-Z element, and the next-to-lightest isotope would then have a half life of $\sim 10^{14}$ years. For Dy, Er, Yb, Hf, Pt, and Pb this possibility is apparently eliminated by the new Bonner Durchmusterung,[21] and for Os and Hg by alpha systematics.

Reference has been made earlier to the observation of pleochroic halos of anomalous radius by Joly and others. Joly[60] believed that they were due to what would now be called extinct natural alpha emitters. He proposed the name *Hibernium* for the responsible element. Henderson,[61] however, has summarized the evidence, including his own observations, and concluded that Joly's interpretation is far from established. Since the radii of the anomalous halos are small, corresponding to short-range alpha particles, the responsible element would have to be lighter than the natural radioactive families. The nuclear data available now, with the considerations of the preceding paragraph, make Joly's postulate seem even more unlikely.

(2) *Even-Z, even-N negatron emitters*. Several unknown nuclides in this class lie just outside of the region of stability. Since all of their nuclei have zero spin and even parity, a knowledge of the characteristics of the decay product, which is usually a short-lived negatron emitter, enables predictions to be made regarding the character of the ground-state transition of the parent. If the energy available is low, this will usually be the only transition which can occur.

Until recently, Fe^{60} was considered an excellent possibility.[97] Very recently, however, Roy and the author[100] have found that this nuclide has a half life of $\sim 3 \times 10^5$ years, which, though not inconsistent with the predictions, is too short. Roy has also shown that S^{38} is a short-lived radionuclide.[101]

Perhaps the best remaining possibility in this class is Hf^{182}, which would decay through Ta^{182} to W^{182}. Ta^{182} has two isomers whose spin difference is probably three. Although neither state has been characterized completely, the absence of beta decay from the ground state of Ta^{182} to the ground state of W^{182} indicates that this transition is at least second forbidden. The decay of Hf^{182} to the ground state of Ta^{182} must be of the same character. If the energy of this transition is less than the excitation energy of the Ta^{182} isomer, 0.180 Mev, Hf^{182} would have to be a second-forbidden beta emitter of very long lifetime. Hafnium always occurs in nature as a minor constituent of zirconium-containing minerals, and most of these minerals should be relatively free of tungsten.

Among the fission products is a 2-minute Se^{84}, whose mass number assignment seems to be adequate. Since Se^{84} is only moderately removed from the beta-stability limit, however, and since its stability should be enhanced by its 50-neutron closed-shell configuration, one would expect it to be somewhat longer-lived. Perhaps the 2-minute Se^{84} is an isomer of a long-lived ground state. In order to have escaped detection among the fission-product selenium isotopes, Se^{84g} would then have to have a half life considerably longer than that of the 6×10^4-year Se^{79}, also a fission product. If Se^{84} should be an extinct natural radionuclide, its detection would be facilitated and its importance increased by virtue of the fact that the potential stable decay product, Kr^{84}, is an isotope of a noble gas element. In fact, the sensitivity of detection would be such that a half life as low as 2×10^7 years might conceivably be sufficient for Se^{84} to exhibit extinct natural radioactivity.

Other possible nuclides in this category are Ti^{52}, Cr^{56}, Pt^{200}, and Hg^{206}, although none appears to be as close to the beta-stability limits as Hf^{182}. Jones[102] has established half life exclusion limits for Ti^{52} of 1 day to 50 days, but believes it is short-lived. For Cr^{56}, Jones's exclusion limits are 2 hours to 200 years, and he believes that it is long-lived. It would decay through Mn^{56} to Fe^{56}, but because of the high isotopic abundance of Fe^{56} (91.6 per cent) and the common occurrence of iron in chromium minerals, it might be difficult to find chromium minerals sufficiently low in iron to permit detection of any radiogenic Fe^{56}. Pt^{200} would yield Hg^{200}, and geochemical fractionations should be adequate. Hg^{206} would go to Pb^{206}, but detection would be impossible because of the natural variations of lead isotope composition.

(3) *Even-Z, even-N electron capturers.* Most of the nuclides of this category that are close to stability have been characterized. Hg^{194} does not appear to be particularly close to the stability limit, but the fact that it is unknown is probably due to a long lifetime. The decay of its daughter, Au^{194}, to the ground-state of Pt^{194} is unobserved and therefore forbidden,

and the decay of Hg^{194} would be similarly forbidden unless low-spin excited states intervene.

(4) *Odd-Z, odd-N nuclides.* All nuclides of this type with mass number greater than 14 are beta-labile, usually with large disintegration energy. Most of the very long-lived members are flanked on both sides by stable isobars, and most nuclides in this class are known. The most prominent unknown odd-odd nuclide is Bi^{208}, which must have a very long lifetime.[103] Its calculated[104] alpha disintegration energy is 3.44 Mev, which would correspond to a half life much greater than 10^9 years. It is calculated[104] to be stable against negatron emission, so it must decay by electron capture to Pb^{208}, for which the calculated[104] energy is 2.93 Mev. The long lifetime can be explained easily by a high spin and the absence of low-lying levels in Pb^{208}. However, even should the half life of Bi^{208} be close to 10^8 years, detection as an extinct natural radionuclide would be impossible because of the isotopic variability of natural lead.

Segrè[105] has discussed the possibility of nearly stable technetium isotopes, concluding that Tc^{97} and Tc^{98} are probably very long-lived. Tc^{97} has subsequently been found[106] to have a half life of 10^4 to 10^5 years, and very recently Tc^{98} has been discovered[107, 108] and found to have a half life of $\sim 10^4$ years.[108] It has also been established[107] that there are no other long-lived isotopes of technetium except for the well-known Tc^{99} (half life 2.1×10^5 years). Consequently, indications[109, 110] of natural terrestrial occurrence of Tc^{98}, or of any macroscopic technetium, require careful examination for alternative explanations. The occurrence of substantial quantities of technetium in certain stars[111] must evidently be the result of current or recent production rather than the residue of a primordial supply several billion years old.

Arnold[10] has suggested that a number of the known odd-odd nuclides may be isomeric states of unknown nuclides of high spin and quite long lifetime. Thus, the fact that activities are known corresponding to nearly all positions between pairs of beta-stable isobars does not mean that the possibility of occurrence of an $\sim 10^8$-year member of the class under discussion is insignificant. One recalls that to the group of naturally occurring odd-odd nuclides consisting of K^{40}, V^{50}, La^{138}, and Lu^{176}, there has very recently been added[29, 30] Ta^{180}. In retrospect its analogy to Lu^{176} is striking, but no one had suspected its existence because of the well-known 8.15-hour Ta^{180}, now presumed to be the metastable isomer.

Accordingly, the argument of Rankama[112], that the existence of a 7-day Cs^{132} precludes the existence of a long-lived Cs^{132} as claimed by Wahl,[52] is not valid. Cs^{134} possesses isomers, of spin-parity 4+ and 8–.[113]

Hence, a high-spin and long-lived isomer of the 7-day Cs^{132}, whose spin-parity is probably 2+ or 3+, seems like an excellent possibility. The different results of Wahl[52] and of Hahn *et al.*[53] respecting radiogenic Ba^{132} in pollucite might then be explained by the assumption that Wahl's specimen was much older than that of the other investigators. The detectability and consequently the value of an extinct natural isomer of cesium of mass number ≤ 132 would be enhanced because it should decay, at least in part, to an isotope of xenon. This possibility has to be discounted somewhat by the observation of Wasserburg and Hayden[47] that no abnormality was noticed in the xenon extracted from a chondritic meteorite.

Another long-lived odd-odd nuclide which was unsuspected for a long time is the Al^{26} ground state. The first crude determination of the half life yielded $\sim 10^6$ years,[59] but according to a subsequent indication it may be somewhat lower.[114] Theoretical estimates of the half life are 10^4 to 10^6 years[115] and 4×10^4 years,[116] so it seems very unlikely that it could be an extinct natural radionuclide. This suggests, however, that a very long half life may occur in an odd-odd nuclide that is not flanked on both sides by stable isobars, and this greatly increases the number of prospects for the occurrence of half lives of the order of 10^8 years.

(5) *Odd-A negatron emitters.* Few of these that are close to stability remain uncharacterized. There has been some evidence for a 23-hour V^{53}. Sheline *et al.*[117] have made several attempts to observe it under favorable conditions, without success. Apparently V^{53} is still unknown. Like V^{51}, it should have spin-parity 7/2−, while its decay product Cr^{53} has a 3/2− configuration, so the ground-state transition of V^{53} should be second-forbidden. Unfortunately, its energy is probably too great for a half life of $\sim 10^8$ years, particularly because excited states may intervene.

Several of the artificially produced radionuclides shown in FIGURE 3 as having half lives of 10^6 years or greater are in this class. Since half lives in this range are difficult to measure, it is pertinent to inquire whether any could be sufficiently in error on the low side for a true value $\gtrsim 3 \times 10^7$ years. The I^{129}, Cs^{135}, and Be^{10} half lives seem to be well determined. The second-longest-lived artificial beta emitter, Pd^{107}, has a half life tabulated[1,2] as $\sim 7 \times 10^6$ years. Unfortunately, this determination[118] has not been published, so it cannot be evaluated. The negatron energy is given[2] as 0.035 Mev. In the measurement of long-lived beta emitters of very low energy there is a tendency to underestimate absorption, and consequently to err on the high side of the half life. On the other hand, it is conceivable that the true half life could be longer.

Urey[119] has pointed out that palladium is siderophile and silver is chalcophile, making iron meteorites favorable hosts for radiogenic Ag^{107} resulting from extinct natural radioactivity of Pd^{107}.

(6) *Odd-A electron capturers.* For some time La^{137} was regarded as a possible extinct natural radionuclide.[97] Ketelle[120] has now found that its half is $\sim 2 \times 10^5$ years.

An excellent prospect is Pb^{205}. Coryell *et al.*[121] have made an intensive search for it, and from their failure to detect K X-rays they conclude that it must be incapable of capturing K electrons. Since it is extinct, it must then transform to Tl^{205} by capture of L- or higher-shell electrons. Huizenga and Stevens[98] have set a lower limit of 3×10^5 years for the L-capture half life. Shaw and Prescott[122] give $\sim 10^6$ years as a lower limit for electron capture, but do not state whether this applies to L-capture or only to K-capture. They predict that the ground state transition is of the technically first-forbidden but strongly *l*-forbidden type, explaining the long lifetime. Some galenas have very low thallium contents,[123] facilitating the detection of radiogenic Tl^{205}

According to the writer's beta stability diagram,[35] Pt^{193} is very close to the line of beta stability and should, therefore, have a very low disintegration energy. Accordingly, it has seemed that the 4.3-day platinum activity emitting 1.5-Mev gamma radiation, assigned by Wilkinson[124] to Pt^{193}, could not be the ground state of this nuclide. Subsequent study[125] has established that this activity results from an isomeric transition. Accordingly, the ground state isomer is still unknown, and because of the failure of others to observe it, it must be long-lived. Its neutron configuration should be $p_{1/2}$, and the proton configuration of its decay product Ir^{193} is $d_{3/2}$, so the transition is probably a first-forbidden one. Because of the probable low energy, Pt^{193g} may accordingly be very long-lived.

Another noble metal nuclide that is unknown is Ir^{189}, which would decay to Os^{189}. Again a first-forbidden transition is expected. A disadvantage in both of the cases Pt^{193} and Ir^{189} is that the geochemical similarity of the parent and daughter would make detection of a radiogenic excess of the latter extremely difficult.

POTENTIAL SIGNIFICANCE OF EXTINCT NATURAL RADIOACTIVITY

Effects Due to Energy Evolution

The contribution of radioactivity to the heat of the earth must be diminishing gradually because of the decay of the most important sources, U^{238}, Th^{232}, K^{40}, and U^{235}. Three billion years ago, the heat from known natural radioactivities was approximately double what it is now, and before that the rate of change was much more rapid because of the significantly greater contributions of K^{40} and U^{235}. If the earth has existed long enough, it must have been kept in a nearly completely molten state by radioactivity up to a certain time a few billion years ago. According to present knowledge of radioactivity, this time was sufficiently remote to cause no conflict with the present views of geologic history. The general subject of radiogenic terrestrial heat has been reviewed several times recently.[8, 58, 126-130]

Several years ago, when experimental evidence seemed to indicate that the half life of K^{40} is as short as $(2.4 \pm 0.5) \times 10^8$ years, it was pointed out[131] that this would have very serious geophysical consequences, since it implied an enormous heat production as recently as 1.5×10^9 years ago, in apparent contradiction to the geological evidence. This conflict has now been resolved by revisions in the radioactive constants of potassium, but the question arises whether a limit to the antiquity of a permanent crust on the earth may have been determined by an as yet unknown and now extinct natural radioactivity. The idea of such an additional early heat source is a common one, but few of those who have proposed it[55,56,58] realized the very special requirements that the responsible nuclide would have to fulfill.

Rosenblatt[56] has given an interesting discussion of possible consequences of a very strong heat source early in the history of the earth. He feels that U^{236} might have provided such a source. However, quantitative considerations make it quite unlikely that the half life, 2.4×10^7 years, is long enough for U^{236} to be of geothermal importance. The decay of U^{236} to Th^{232} releases 4.6 Mev, whereas the decay of U^{238} to Pb^{206} liberates about 52 Mev, of which perhaps 5 Mev escapes in the form of neutrinos, leaving about 47 Mev in the earth. Considering that the disintegration constant of U^{236} is nearly 200 times that of U^{238}, U^{236} is about 18 times as effective a heater as U^{238} on a mass basis. Postulating, as does Rosenblatt, that roughly equal quantities of the two isotopes were created initially, the heat generation by U^{236} would decay to equality with that from U^{238} in about 100 million years. Thus, considering the additional heat generated by other radionuclides, U^{236} would be relatively unimportant after the first 100 million years of the universe. Though there is no direct evidence to the contrary, the discussions of Gamow[83] make it seem unlikely that the earth or the moon, which was also considered by Rosenblatt, could have been formed in a time so short that the heat production by U^{236} could be significant in their history.

Urey[58] believes that melting must have occurred in the bodies (planetesimals, asteroids?) from which the meteorites and planets were derived, in order to account for the silicate minerals and metallic phase of meteorites and for the differences in chemical composition among the minor planets, and that the radioelements K, Th, and U were insufficient to accomplish the necessary heating. He suggests that the accretion of these objects may have occurred within some 10^7 years after the synthesis of the elements, and that one or more of the radionuclides with half lives of some million years may have been important sources of heat in them. Of the known nuclides with half lives of this order of magnitude, only Al^{26} seems to Urey to have the right combination of half life, disintegration energy, and primordial abundance, and he postulates a history of the solar system in which Al^{26} plays an essential role. Urey seems, however, to have overestimated the primordial abundance of Al^{26} by a factor of ~ 50. (A reasonable guess as to the primordial Al^{26} abundance is ~ 1 per cent of the Al^{27} abundance,[132] giving ~ 0.015 per cent as the weight fraction of Al^{26} in chondrites; Urey assumes 0.75 per cent.) Moreover, he overlooked the approximate nature of the value $\sim 10^6$ years for the Al^{26} half life.[59] As stated above, the true value is probably lower. Hence, Al^{26} can hardly have had the effects imagined. Urey does mention the possibility that some other at present unknown nuclide might have been responsible for these effects.

From the result of Wasserburg and Hayden[47] on meteoritic xenon, such a nuclide would probably have to have a half life at least as long as that of I^{129}. From Gamow's estimate[83] on the time requirement for condensation of matter, the half life would probably have to exceed that of U^{236}. If there is such a nuclide, Rosenblatt's and Urey's discussions would be quite appropriate to it. We may ask whether Sm^{146} could have been of importance. Its disintegration energy is 2.6 Mev,[84] and its primordial cosmic abundance[132] may have been 10 times that[58] of U^{238}. If its half life should be exactly the value estimated,[84] 5×10^7 years, its energy would have exceeded that of U^{238} for the first $\sim 3 \times 10^8$ years. It is at best a borderline case. The same applies to Pu^{244}.

To be important as a heater, an extinct nuclide would in addition have to be an isotope of one of the lighter and more abundant elements. Before the half life of Fe^{60} was known, calculations based on an assumed half life of 10^8 years and an assumed primordial isotopic abundance of 1 per cent showed that it would have had an enormous heating effect for over 10^9 years after nucleogenesis.[8] Consider a hypothetical nuclide of half life 10^8 years, disintegration energy 1 Mev, mass number ~ 50, and primordial cosmic abundance corresponding to 0.1 per cent of the elements in chondrites. Its initial mass abundance would then be about 30,000 times that of U^{238} and its specific heat production rate about 6 times as great. Initially, its total heat production rate would then be about 180,000 times that of U^{238}. For a considerable period of cosmic time, it would be the major source of radiogenic heat. After 3×10^8 years, when planets may have been forming,[83] it would yield about 20,000 times as much heat as U^{238}. At 10^9 years this proportion would be about 200, and it would not drop to unity until about 1.7×10^9 years. After two billion years its contribution would be relatively insignificant. If the half life should be 2×10^8 years, its heat production would not drop to equality with U^{238} until about 3 billion years after the creation.

It can be seen that an extinct radionuclide of moderate primordial abundance and specific energy release could have important thermal consequences if its half life were of the right order of magnitude. The probability of existence of a nuclide meeting all three requirements, however, must be regarded as quite small.

A discussion of radiation damage effects would parallel the above quite closely. However, such effects produced very early in the earth's existence would be extremely unlikely to escape obliteration and survive to the present.

Determination of the Age of the Elements

From the discussion given earlier, it is apparent that the age of the universe, if there is a definite age, is known only very approximately. Moreover, it is not at all certain that the nucleogenic event which gave rise to our present local supply of elements occurred simultaneously with the start of the nebular recession. This supply may have been formed, or at least altered in composition, at some subsequent time, as for example in the interior of a star, prestar, nova, or supernova,[133, 134] or it may be a mixture from various sources. Although samples of meteoritic uranium[135] and potassium[136] were found to have the same content of U^{235} and K^{40} as their respective terrestrial counterparts, suggesting a common origin, this represents too limited a sampling of the universe for generalization of this conclusion. A different history for at least some matter is indicated by the fact that some S-type stars have spectra showing strong lines of technetium,[111] whose long-lived isotopes have half lives of less than a million years. Evidence of a related type is the high and variable C^{13}/C^{12} ratio found in R- and N-type stars[137] and the general variation in relative abundances of heavy elements in stars.[133]

Thus a fairly accurate determination of the age of the elements accessible to us would be of great interest, whether or not it could be identified with the age of the universe itself. Brown[46] has proposed a method for doing this based on what is here called extinct natural radioactivity. Assuming that meteoritic phase separations took place early in the life of the elements, the interval between the formation of the elements and the separation of the phases might be estimated by determining the isotopic composition in two or more phases of elements containing the decay products of radionuclides of intermediate lifetime. If no variations were found in a case of a parent and daughter which were chemically fractionated, one could set a lower limit to the interval of a few half lives of the parent. If variations were detected, an upper limit of a few half lives could be set. If a series of such limits could be determined, it might be possible to evaluate the interval in question fairly closely. The total age of the elements would be given by adding to this the interval since the phase separation, determined by the conventional methods used for terrestrial minerals, particularly those based on the transformations of primary natural radionuclides.

Brown and Inghram[138] made a test on copper in an iron meteorite, before it was known that the half life of Ni^{63} is only 85 years. The first significant application of the method has just been made by Wasserburg and Hayden,[47] who examined the Xe^{129} content of xenon from a chondrite. From the absence of detectable radiogenic Xe^{129}, a lower limit to the interval between nucleogenesis and xenon retention by the meteorite is between 17.4 and 23.7 half lives of I^{129}, depending on the iodine concentration, or between 3 and 4×10^8 years. Because of the possibility of xenon loss by diffusion, they adopted 2×10^8 years as a conservative limit. Combining this with their A^{40}/K^{40} age of the same meteorite, $(4.8 \pm 0.2) \times 10^9$ years,[71] they obtained as a lower limit for the time since the formation of the elements 5.0×10^9 years. [The meteorite age was calculated[71] using a geochemically estimated electron-capture disintegration constant of K^{40} corresponding to an A^{40}/Ca^{40} branching ratio of 0.085. Recalculation using only physically determined disintegration constants (TABLE 1) yields 4.4×10^9 years for the time since argon retention. The minimum age of the elements in thus 4.6×10^9 years.]

If a difference in isotopic composition could be detected in even a single case, it might be possible to obtain a fairly precise estimate of the time of phase separation, instead of just a limit. This would require estimation of the primordial abundance of the parent nuclide. Suess[66] has pointed out that, in the isotopic and cosmic abundances of the nuclides, there are a number of regularities and correlations with known features of nuclear structure, from which it is possible to estimate the primordial abundance of a great many near-stable nuclides with a fair degree of accuracy, perhaps within a factor of two. An uncertainty of this order of magnitude would result in an uncertainty of only one half life in the time of separation. Even if clean-cut separations between the parent and daughter elements did not occur, the time of fractionation might be calculated by application of the method proposed by Wickman[139] for use on multiphase materials such as igneous rocks.

Suess,[43] Katcoff, Schaeffer, and Hastings,[44] and Suess and Brown[45] used a similar method to obtain from the transition of I^{129} to Xe^{129} information about the age of the elements when the earth began to retain an atmosphere. Here only one phase, the earth as a whole, is available for examination, and there are insufficient data to determine whether some of the present terrestrial Xe^{129} has been produced by radioactive decay of I^{129} since the loss of the bulk of the xenon. In principle, a prediction of the primordial abundances of I^{129} and Xe^{129} would permit a solution, but the accuracy of this prediction would have to be much greater than the accuracy required in a case where two phases can be examined. Accordingly, although Katcoff *et al.* made such a prediction, and calculated that the elements were 2.7×10^8 years old at the time in question, Suess and Brown have pointed out that, because of uncertainties, the data actually yield only a lower limit of 4×10^8 years for this age.

A natural extension of the method of Brown would be to terrestrial minerals. As has been discussed earlier, the probable later time of formation of obtainable terrestrial materials would be a disadvantage, but the greater variety and degree of chemical fractionations occurring in the heterogeneous environments on the earth's surface would be a distinct advantage. A further advantage is that minerals formed at different epochs can be obtained. If the radiogenic daughter of an extinct natural radionuclide should occur in minerals of a given element, its amount (corrected in the usual way for any nonradiogenic portion originally present in the mineral) relative to any surviving isotope of the parent element would be an exponential function of the age of the mineral. If this ratio and an independent age of each of several such minerals could be determined simultaneously, it would be possible to plot a "cosmic decay curve" for the extinct radionuclide. FIGURE 4 shows schematically how the measurements might be plotted on the conventional semilogarithmic coordinate system, and the cosmic decay curve thereby established. From this curve, the half life of the nuclide could be determined in the usual manner. Alternatively, if the half life were known from laboratory investigations, giving the slope of the semilogarithmic curve, only one positive observation of the decay product in a dated mineral would be needed to establish the position of the curve. This curve is one of the family shown in FIGURE 2. Extrapolation of the curve back to the estimated primordial abundance of the decaying nuclide relative to its reference isotope would give the time since the origin of the elements with a fair degree of precision.

Establishment of an Accurate Early Geochronometry[140]

The functional relationship just mentioned, between the age of a mineral that once contained an extinct radionuclide and the quantity of radiogenic product, suggests what might well be the most important consequence of extinct natural radioactivity: a method for determining with relatively high precision the ages of extremely old minerals. This would greatly facilitate working out the early events of geologic history, about which relatively little is known at present.

The measurements by themselves would provide a relative time scale, comparable to that derived from stratigraphy. Accurate comparisons could be made of the relative times of events occurring in widely separated parts of the earth. A determination of the half life of the parent nuclide would convert this to an absolute time scale, though of indefinite origin. It would remain to date a single point on this scale by conventional methods to link the new scale to that extending back from the present. Since the early scale would thus be fixed relative to the present, it would not depend on any assumption regarding the primordial abundance of the nuclide employed nor on any postulate regarding the origin of the elements.

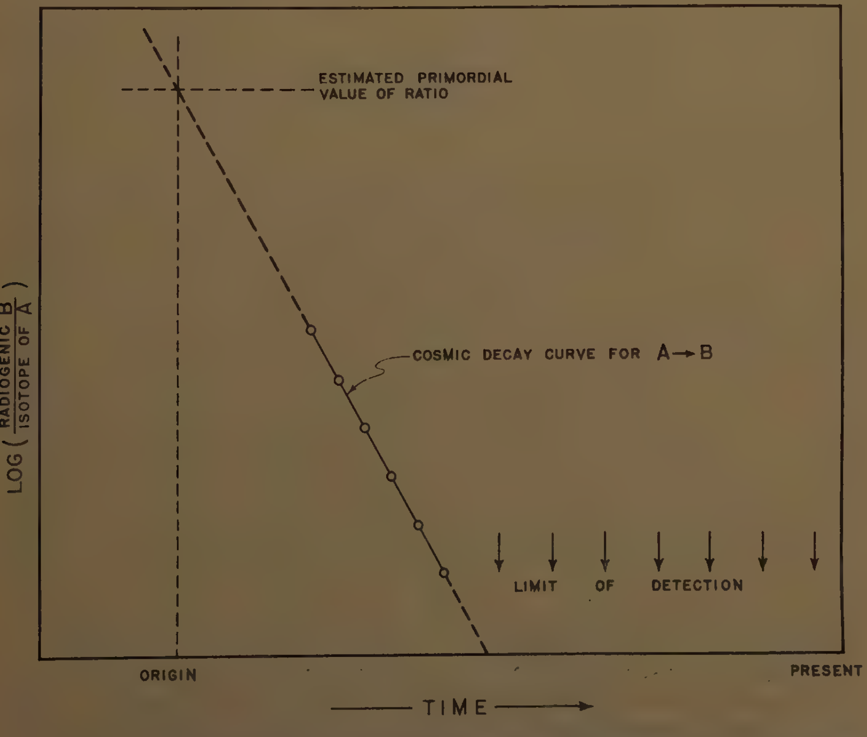
ESTIMATED PRIMORDIAL VALUE OF RATIO
COSMIC DECAY CURVE FOR A→B
LIMIT OF DETECTION
LOG (RADIOGENIC B / ISOTOPE OF A)
ORIGIN
PRESENT
TIME →

FIGURE 4. Schematic diagram of hypothetical observations on the decay product of an extinct natural radionuclide, illustrating application to determining the age of the elements and to dating early geologic events.

A point worthy of note is that this method of geochronometry would be more and more precise for older and older minerals, since the minerals formed earlier would have larger residual amounts of the unstable nuclide, and the variation with time would be more rapid. For this reason, it would nicely complement the existing methods, which are capable of fairly high precision for recent events, but whose early dates are subject to very large uncertainty.

In order for the method to be applicable, both the extinct nuclide and its decay product must have at least one stable or very long-lived isotope. The isotope of the extinct nuclide is necessary as an indicator of the amount of the latter which could have been present in the mineral in past times. The isotope of the decay product is necessary in order to enable a radiogenic excess to be recognized, and to determine the amount of nonradiogenic contaminant to be subtracted. Then, if a plot such as that of FIGURE 4 is available, from a measured value of the age index ratio the time of mineralization can be read directly off the cosmic decay curve.

The half life requirement for a nuclide to be useful in this manner is somewhat more stringent than for mere detection as an extinct natural radionuclide. For detection we have been taking as the lower half life limit 1/10 of the time between formation of the elements and formation of chemically fractionated materials. For geochronological application, the nuclide would have to survive until somewhat later than the beginning of formation of accessible rocks and minerals. Ages of rubidium-containing minerals ranging up to $\sim 4 \times 10^9$ years have been reported.[141] If these are correct, if the elements are 5×10^9 years old, and if the method is to be applicable for a 10^9-year period of geologic time, the half life might have to be at least 2×10^8 years. However, the above-mentioned strontium ages were calculated using a Rb^{87} half life of about 6×10^{10} years. There are some indications[12, 14, 8] that it may be somewhat lower, perhaps around 4×10^{10} years. The extreme strontium ages would then be reduced to $\sim 3 \times 10^9$ years. The oldest minerals considered to be reliably dated by the lead method are also about 3×10^9 years old.[142] If this is the true upper limit to the antiquity of accessible terrestrial materials, then a useful extinct natural radionuclide would have to have a half life fairly close to 3×10^8 years. For the special case of a nuclide yielding a noble gas decay product, the half life might need to be only about half of the corresponding value indicated above.

A further requirement is, of course, that the parent and daughter elements be geochemically fractionated. If both were rare earth elements, this condition would not be fulfilled, and the same would probably be true if both were platinum group elements. Thus, even should Sm^{146} have the optimum half life, it would be useless geochronometrically.

Because of the stringency of the qualifications for a nuclide to be useful for this purpose, one can not be very optimistic about the possibility that a suitable nuclide may exist.

AN EXPERIMENTAL PROGRAM

A program of investigation is under way at the Carnegie Institute of Technology to find whether any extinct natural radionuclides exist. The first aspect of this program is an attempt to produce artificially nuclides for which long lifetimes are expected on theoretical grounds. The second aspect is the isolation, from minerals which may have contained such nuclides, of the potential daughter elements for examination of their isotopic composition.

For the production of long-lived radionuclides, the 400-Mev proton synchrocyclotron of the Carnegie Nuclear Research Center is available. Although the beam current of such a machine is lower than that of conventional cyclotrons, the greater particle energy often more than compensates by virtue of larger cross sections, increased target penetration, and greater variety of products. Still, the longest lifetimes that can be found in such bombardments range from ~ 1 to $\sim 10^6$ years. Nuclides having lifetimes sufficient for extinct natural radioactivity could hardly be detected. Nevertheless, this is an important means of screening the various possibilities. Those that are found to be short-lived can be eliminated from further consideration, and those for which only lower limits to the half lives can be determined in this manner can be sought further by other means. Results of this program to date on Fe^{60}, S^{38}, Ti^{52}, and Cr^{56} have been mentioned earlier in this paper.

The 60-inch cyclotron of the Sarah Mellon Scaife Radiation Laboratory of the University of Pittsburgh has been generously made available to us on occasion. The discovery and characterization of the long-lived Al^{26} was achieved with the use of this machine.

For production of very long-lived nuclides in amounts sufficient for detection, we are making use of the intense neutron irradiation facilities available in some of the nuclear reactors of the Atomic Energy Commission. This is probably the most favorable means of producing an even-even negatron emitter of the category of interest. Successive capture of two neutrons is necessary. In such a case overwhelming amounts of shorter-lived radioactive isotopes may be produced, preventing direct observation of the activity sought, but in all such cases the latter generates a radioactive isobar, whose chemical extraction provides the means of avoiding the interference.

In the other part of the program, we are employing both terrestrial and meteoritic minerals. Before the determination of the Fe^{60} half life, nickel samples were isolated from a number of pre-Cambrian iron minerals and mineral phases of iron meteorites, and some of them examined mass spectrometrically at the Argonne National Laboratory.[143] Similar tests of barium from a variety of rare earth minerals were made[144] before the La^{137} half life was known.

Work is in progress on the isolation of thallium from geologically old lead minerals to seek evidence of extinct natural radioactivity of Pb^{205}. We plan to extend these investigations to as manv of the possibilities for which suitable minerals can be obtained.

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SUMMARY

An extinct natural radionuclide is defined as a nuclide whose lifetime is too short for detectable amounts to have persisted from the time of nucleogenesis to the present, yet long enough for its decay to have produced effects in nature that can be identified at the present time. Although a number of writers have speculated on various aspects of this type of natural radioactivity, no definite evidence for its occurrence has yet been found. This paper examines the possibility of the occurrence of extinct natural radionuclides and of discovering them, and discusses some consequences of their existence and the kinds of information that might be obtained from their discovery and investigation.

The principal observable manifestation of an extinct natural radionu-

clide would be the occurrence, in a mineral or other geochemical phase that had once contained the unstable nuclide, of its decay product in abnormal isotopic abundance. Heat production early in the history of the earth might be important, but this and other nonspecific effects such as radiation damage and helium production would be difficult to identify and assign. Quantitative considerations indicate that the half life of an extinct natural radionuclide would probably have to be between $\sim 3 \times 10^7$ and $\sim 3 \times 10^8$ years.

A survey of all known long-lived nuclides suggests that there may well be a small number having suitable half lives. Possible types of transitions are: first-forbidden negatron emission of extremely low energy, second-forbidden negatron emission of low energy, third-forbidden negatron emission of fairly high energy, first-forbidden electron capture of very low energy, and second-forbidden electron capture of moderate energy. Alpha emission is also a possibility, but the likelihood is small. Some specific possibilities are discussed.

The consequences of heat evolution by extinct natural radioactivity are considered, following recent discussions of possible effects of U^{236} by D. B. Rosenblatt and of Al^{26} by H. C. Urey. Although these nuclides are apparently too short-lived, a nuclide of somewhat longer lifetime and moderate primeval abundance might have considerable geothermal significance. Applications to obtaining information about the age of the elements by the study of meteorites as proposed by H. Brown and H. E. Suess are discussed, and it is suggested that extension of such studies to terrestrial minerals might offer important additional possibilities. The functional relationship between the age of a mineral incorporating an extinct radionuclide and the quantity of radiogenic product offers the possibility of establishing an accurate chronometry for early geologic history, which would be most accurate for the earliest times.

An experimental program in search of extinct natural radionuclides at the Carnegie Institute of Technology involves attempts to produce long-lived nuclides by artificial means and to detect their decay products in terrestrial and meteoritic minerals.

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